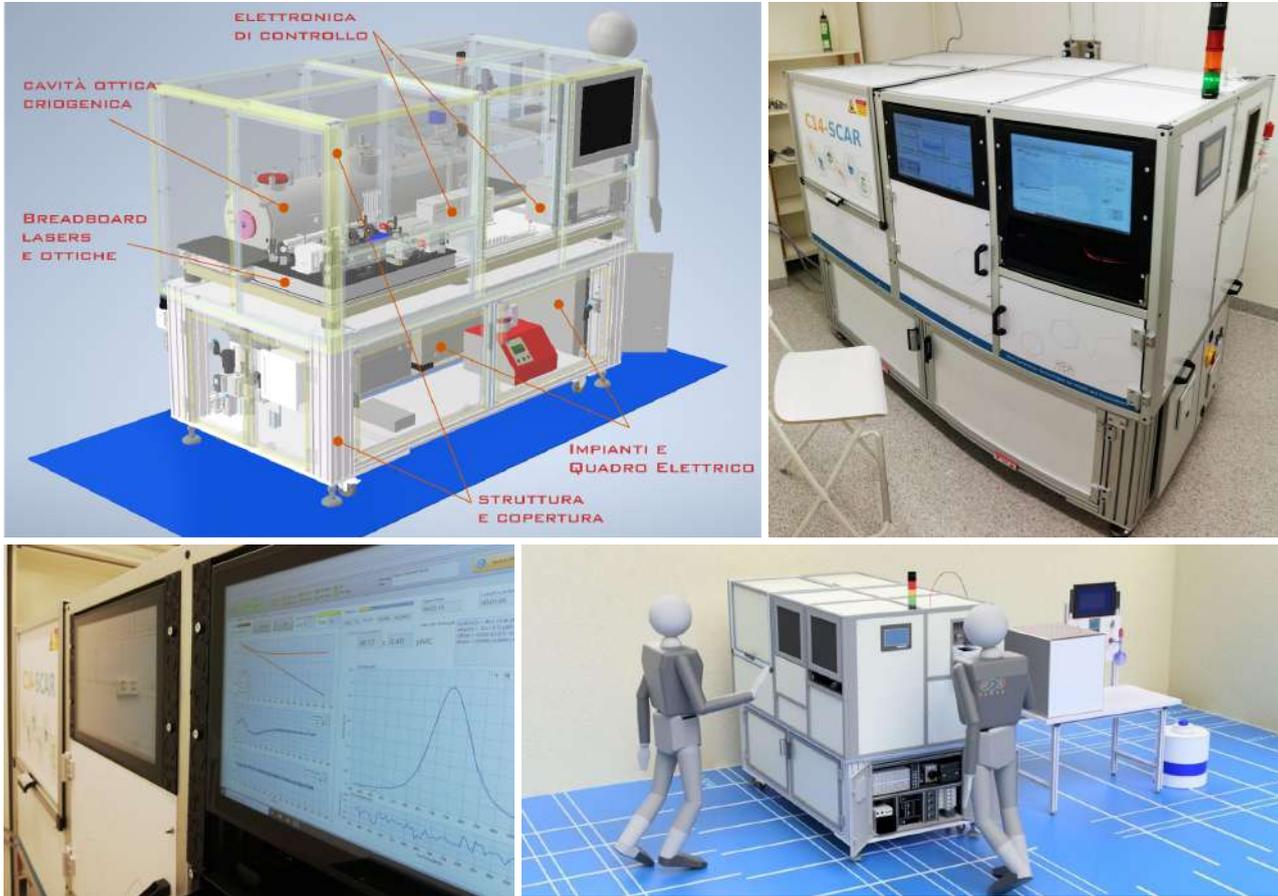# The C14-SCAR Instrument

## Description of the instrument

The C14-SCAR analyzer is an instrument for trace-gas detection by laser spectroscopy, which exploits the technique of cavity ring-down (CRD) in saturated-absorption regime (SCAR). This apparatus is able to detect the radiocarbon contained in a gaseous carbon dioxide sample with a precision approaching accelerator mass spectrometry (AMS). In fact, the achievable precision level in 30 minutes of averaged measurements can be close to 1% of the modern carbon content (1 pMC) and the dynamic range is higher than 5 orders of magnitude (highly enriched samples can be measured, too). The preparation of each sample routinely takes about 30 minutes.

The CRD technique consists in coupling the laser radiation to a high-finesse cavity; once a predetermined filling level has been reached, the laser is rapidly switched off and the radiation coming out of the cavity is detected while decaying exponentially. The time constant of the decay is related to the losses in the cavity. With the empty cavity, the losses are only due to the mirrors; if there is an absorbing gas in the cavity, the decay time is shorter; from the difference of the decay

rates (full/empty) the concentration of the absorbing gas in the cavity can be obtained. This technique, in its simplicity, is very efficient, but requires high-level equipment especially in the region where we want to work, that is in the mid infrared at 4.5 μm. The C14-SCAR system consists of components specifically designed to work at this wavelength, whose main parts are described here.

1. Optical bench

An optical breadboard hosts the laser source, which is composed by 2 quantum cascade lasers (QCLs) with ~100 mW power: one is used to couple infrared radiation to the high-finesse cavity, to perform CRD, and the other one is used as a frequency reference, thanks to the locking to a molecular transition of nitrous oxide. Both of them are driven by our ultra-low-noise current supplies and are protected from feedback by optical
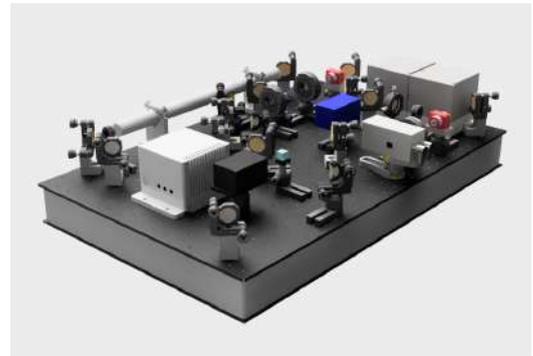
isolators. The locking to the molecular transition is achieved by a differential detection system that exploits polarization spectroscopy. The first laser, used to perform CRD, is coupled to the high-finesse cavity and, to ensure optimal stability of the resonance, it is locked to the cavity by the Pound-Drever-Hall technique. To refer the first laser to the absolute frequency of the second one, a beat note is detected between the 2 lasers, which is maintained at constant frequency by a feedback loop controlling the cavity length. An acousto-optic modulator (AOM) ensures complete switch off of the laser beam for starting each cavity ring-down event.

2. Measurement cell

The optical cavity is the core of the apparatus and it is the most complex and critical part. It has a vacuum system for loading and unloading the gas to measure, several fittings to connect pressure gauges and a vacuum pump and it is equipped with 8 thermistors for the temperature measurement
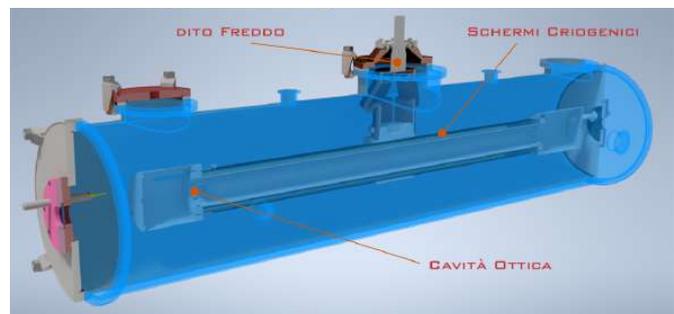
read by a multisensor monitor. It is designed to work at very low temperatures (below 170 K), thanks to the high thermal insulation from the external environment, and it is connected to a cryocooler. Particular attention is paid to the optical mounting of the high-reflectivity mirrors

(optical finesse > 100,000). It is designed to allow both the coarse and fine alignment of the cavity even in cooled conditions, while isolating the mirrors from external vibrations and thermal load. One of the mirrors is piezo-mounted for frequency tunability of the cavity.

3. Signal detection/acquisition stage

The laser beam leaking out of the cavity during each CRD event is detected by a thermoelectrically-cooled mid-infrared photodiode. The photocurrent is processed by a transimpedance preamplifier and sent to a high-resolution (22 bits, 1 MS/s) digitizing oscilloscope which is part of a PXI architecture also including additional modules. A few photodetectors dedicated to the several lockings described above, with specific and suitable characteristics, are hosted by the optical bench.

4. Vacuum apparatus

A turbomolecular pumping station continuously provides the vacuum in the external chamber and is used to evacuate the measurement cell before filling it with a new gas sample. An absolute capacitive transducer measures the pressure of the sample gas with an accuracy close to 0.1%. Auxiliaries pressure transducers are used to measure the pressure in the external chamber and during the sample filling procedure.

5. Cryogenic apparatus

A water-cooled low-vibration Joule-Thomson cryocooler cools the measurement cell down to 170 K. A thermoelectric chiller provides circulating cold water for cooling the cryocooler, the AOM and its RF driver.

6. Elemental analyzer and sample preparation

C14-SCAR can measure only pure CO_2 gas samples. Therefore the carbon content of any solid or liquid sample must be first turned into CO_2 by burning it and purifying all gaseous combustion products from any interfering species, especially from N_2O. Our analyzer is equipped with the best tested elemental analyzer able to perform this task.
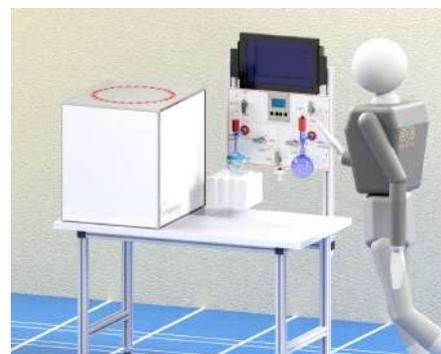

At the gas outlet of the analyzer a simple valve system allows to extract and purify the CO_2 gas produced by the analyzer by freezing it in a LN bath, and then pumping out the unwanted gasses,

in particular the He carrier gas. After that, the gas is ready to be sent to the C14-SCAR instrument for analysis.

7. Software

The C14-SCAR instrument is provided with a GUI software for instrument control, signal acquisition and signal analysis. It is a LabVIEW-based application that includes some Python scripts for analysis. Instrument control code is used to set operative conditions of the analyzer by programmable control of its components: emission parameters of the laser systems and thermodynamic parameters of the measurement cell. Signal acquisition code is used to automatically control the acquisition procedure, including laser locks and scan, SCAR process and decay signal digitization and storage. Signal analysis code provides fit procedures to extract relevant parameters for the determination of the ^{14}C concentration. Results are graphically plotted and automatically stored.
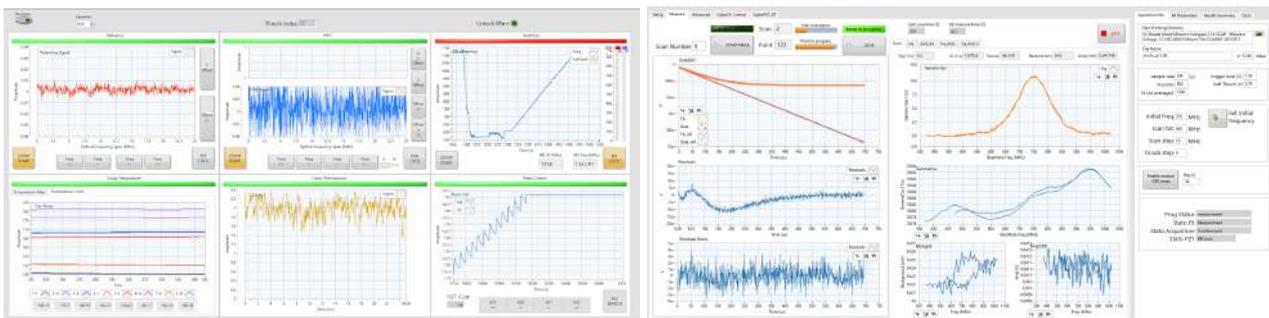

Dual-touch screen interface of the C14-SCAR instrument
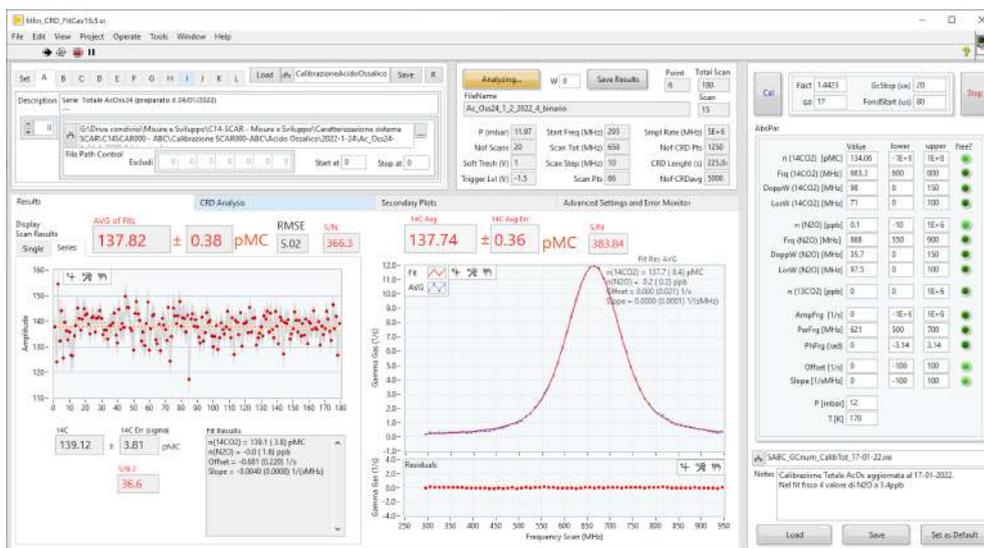
Offline analysis software

Description of the sample preparation process

To be measured by the C14-SCAR instrument, any solid or liquid sample must be converted into pure CO_2 gas. The carbon content of the sample must be enough to fill the measurement cell with a 0.7 L net volume at the optimal pressure of 13 mbar. The required carbon mass is about 9 mg. The elemental analyzer is able to measure the molar fraction of C of the sample, in case its chemical composition is not known a priori. In this way the amount of sample to be burned can be calculated in advance.
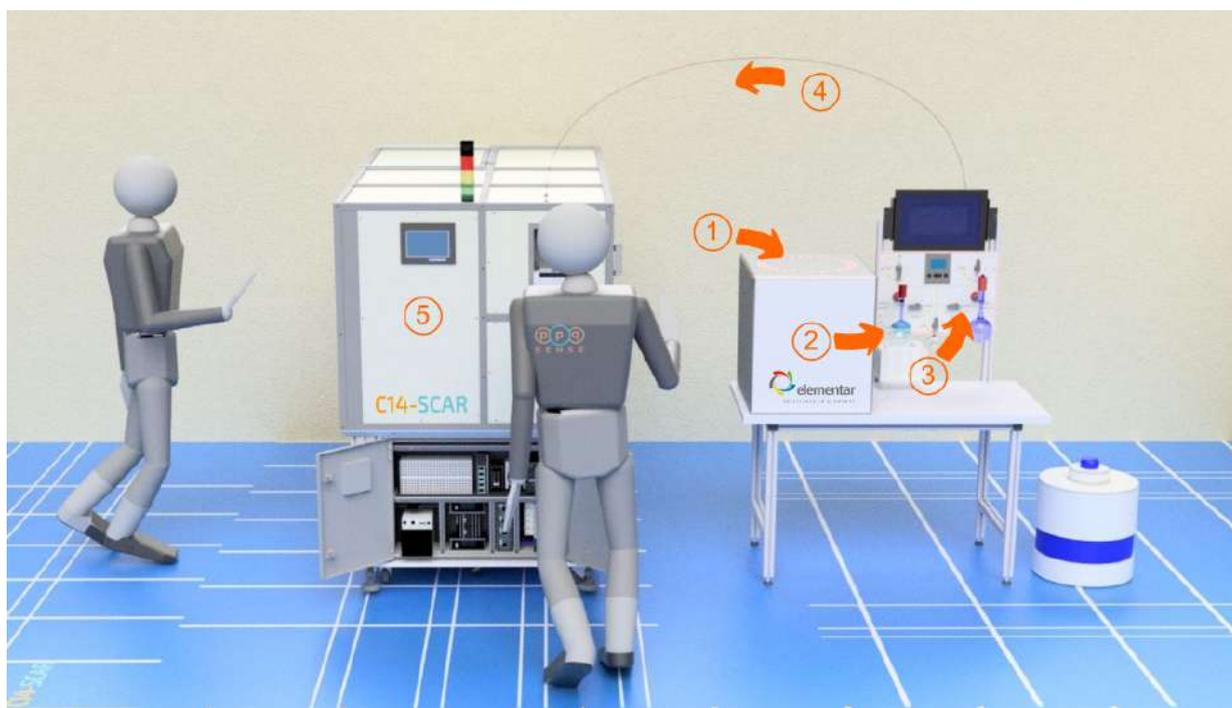
The measurement process starts therefore with the preparation of the sample portion to burn: a few tens of milligrams of the sample are weighted with a precision balance with 0.01 mg resolution and enclosed in a small tin cup that is placed in the loading wheel of the Elemental Analyzer (1). The sample is then automatically introduced into the furnace where the combustion process in an oxygen atmosphere takes place (2). The gaseous combustion products are carried by a He flow through a reduction column and the purge and trap technology is able to purify them from any interfering species, especially from N_2O. At the outlet of the analyzer a simple valve system allows to freeze the CO_2 gas produced by the analyzer in a glass ampoule immersed in a liquid-N_2 bath, and the He carrier gas is pumped out (3). After that, the gas is ready to be sent to the C14-SCAR instrument via an automated procedure (4). Once the transfer of the gas to C14-SCAR is completed, the measurement routine is started (5).

The whole process, from the sample weighting to the results output, takes about 30 minutes.

Examples of materials and applications

Any material containing carbon that can be burned with the above described process can be analyzed by the C14-SCAR instrument. In principle, a CO_2 gas sample can be directly measured, provided that it is pure CO_2 and not a mixture containing traces of other gasses.

The concept of Modern Biogenic and Fossil

The C14-SCAR instrument analyzes the CO_2 gas produced by burning the sample and retrieves the concentration of ^{14}C by measuring the spectral area of a given molecular transition of the $^{14}CO_2$ molecule. If the sample is taken from a modern living being, the measured ^{14}C concentration will be close to the so-called *Natural Abundance* or *Modern Carbon (MC) Concentration*. This corresponds to **100 percent of Modern Carbon**, i.e. **100pMC**. A similar measurement taken on a sample containing only fossil carbon will not show any signal corresponding to the $^{14}CO_2$ transition, since no 14C is present: this corresponds to **0pMC**.

Modern Biogenic Material: 100 pMC	Fossil Material: 0pMC
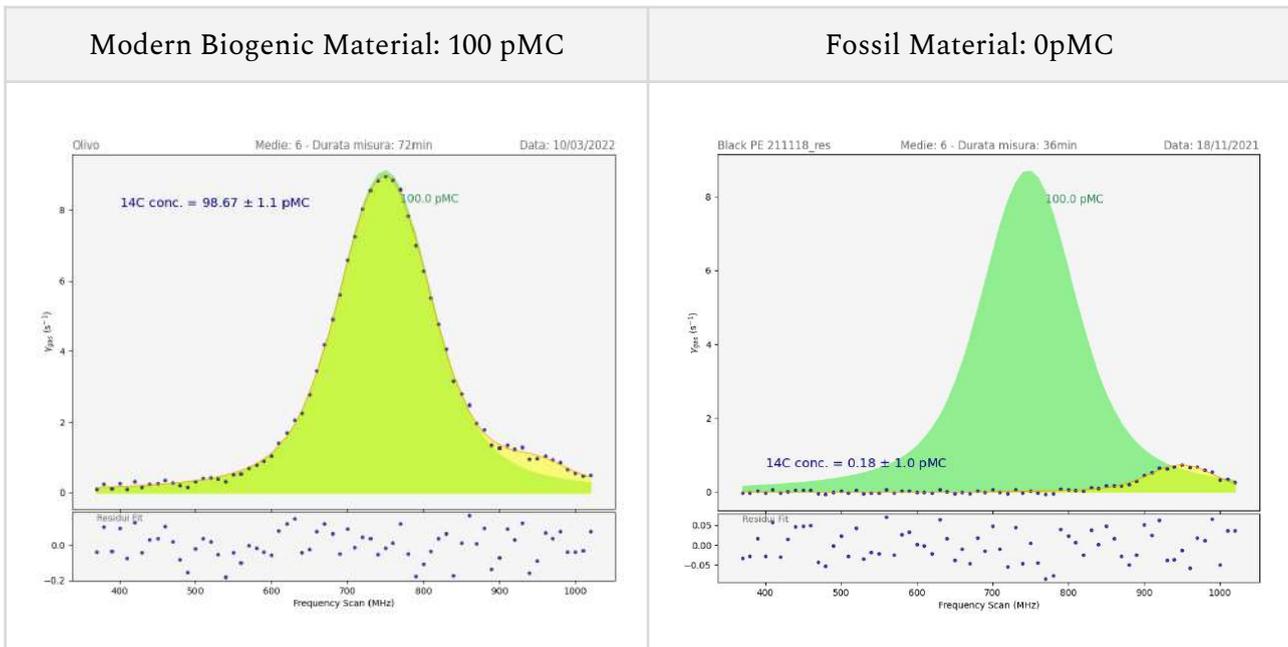
Therefore, any result falling in the range 0pMC - 100pMC will give you **a direct measurement of the bio-based carbon content** of the analyzed material.

This method is totally **matrix-independent**, since the measurement is taken always on the CO_2 gas produced by burning the sample, therefore not depending on the chemical composition of the original material.
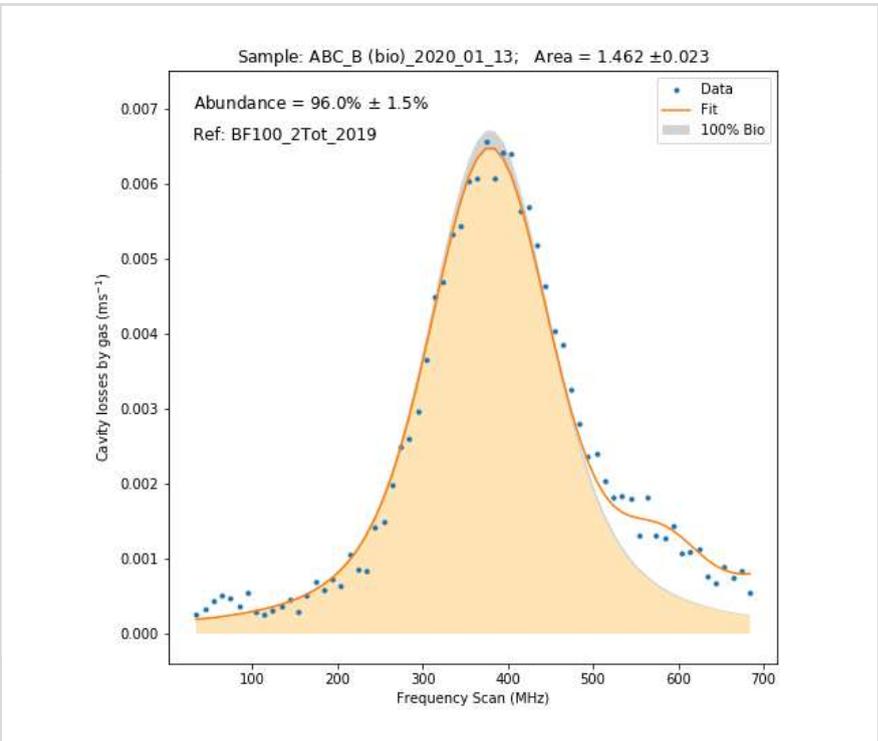
In the following an overview of several analyses performed on a wide range of material is given.

Fuels

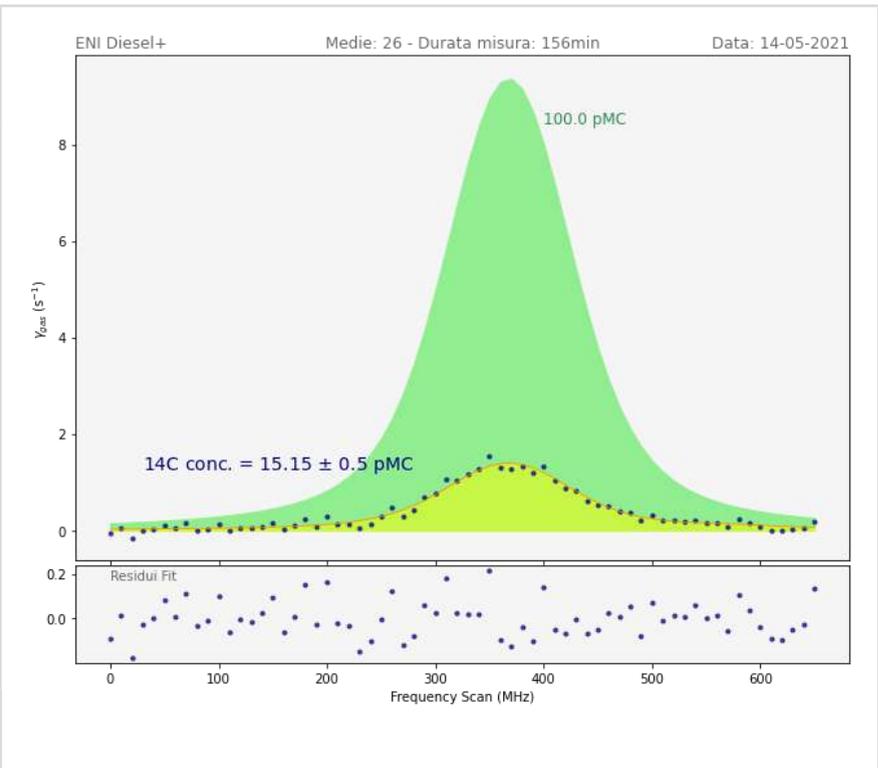## Seaweed Energy Solutions (SES) fuel

courtesy of RISE

Result: 96% bio

Sample: ABC_B (bio)_2020_01_13; Area = 1.462 ±0.023

Abundance = 96.0% ± 1.5%
Ref: BF100_2Tot_2019

- Data
- Fit
- 100% Bio

Cavity losses by gas (ms^{-1}) vs Frequency Scan (MHz)

ENI Diesel+

courtesy of ENI

Result: 15% bio

ENI Diesel+   Medie: 26 - Durata misura: 156min   Data: 14-05-2021

100.0 pMC

14C conc. = 15.15 ± 0.5 pMC

γ_{gas} (s^{-1}) vs Frequency Scan (MHz)

Residui Fit

Plastics

Shopper
courtesy of RISE

Result: 28% bio

Sample: 9F020347-1; Abundance = 28%

- Data
- Fit
- 100% Bio

Frequency Scan (MHz)
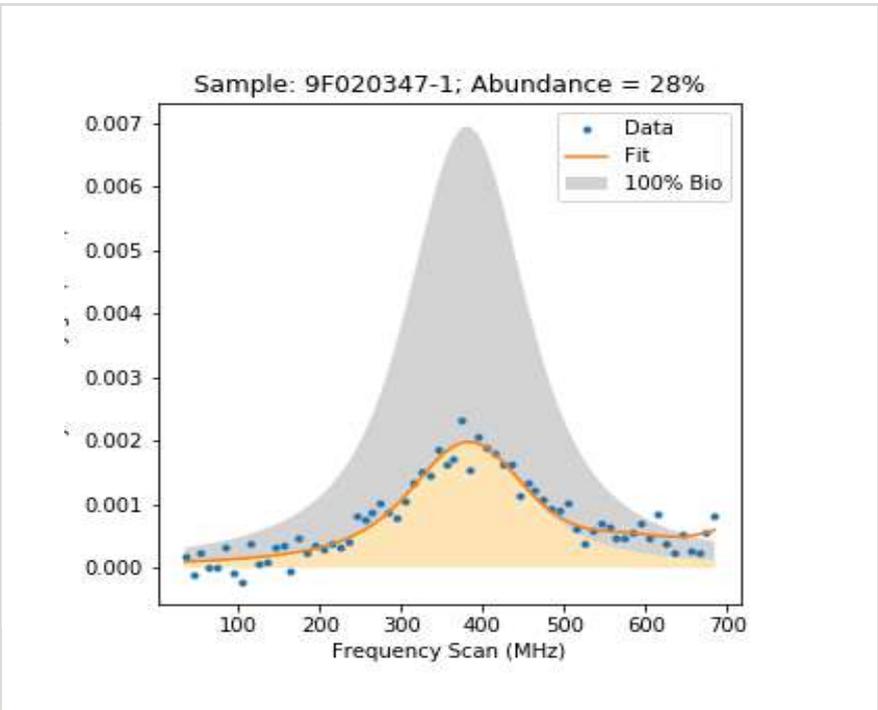
Plastic Cap
courtesy of RISE

Result: 0% bio

Black PE 211118_res   Medie: 6 - Durata misura: 36min   Data: 18/11/2021

100.0 pMC

14C conc. = 0.18 ± 1.0 pMC

Residui Fit

Frequency Scan (MHz)
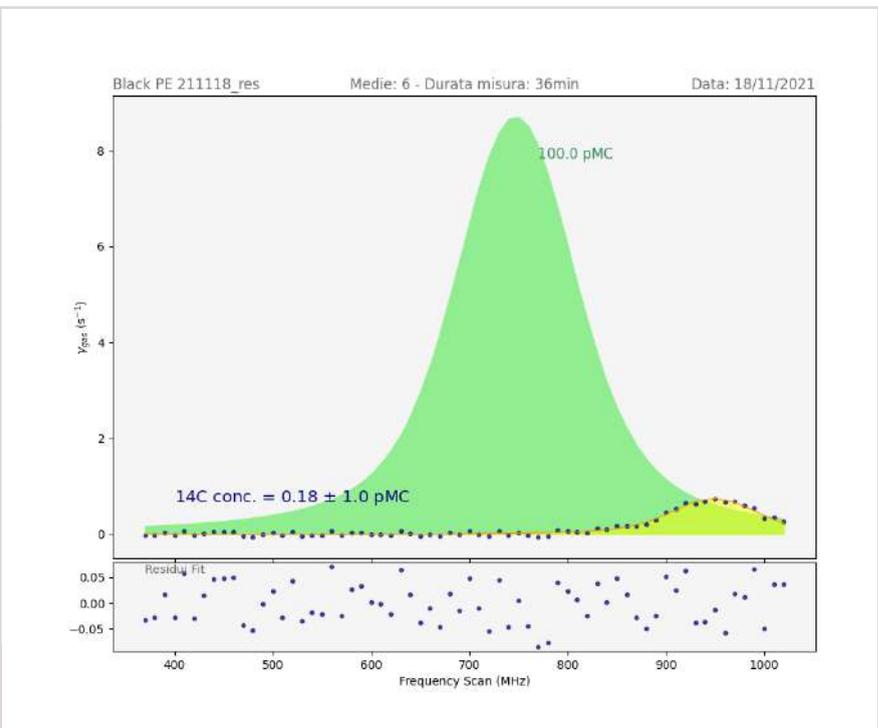
Fabric and Textiles

Linen 100% bio
courtesy of ppqSense

Result: 99% bio

LinoBio Medie: 23 - Durata misura: 276min Data: 10/03/2022

14C conc. = 98.72 ± 0.8 pMC 100.0 pMC

Residui Fit
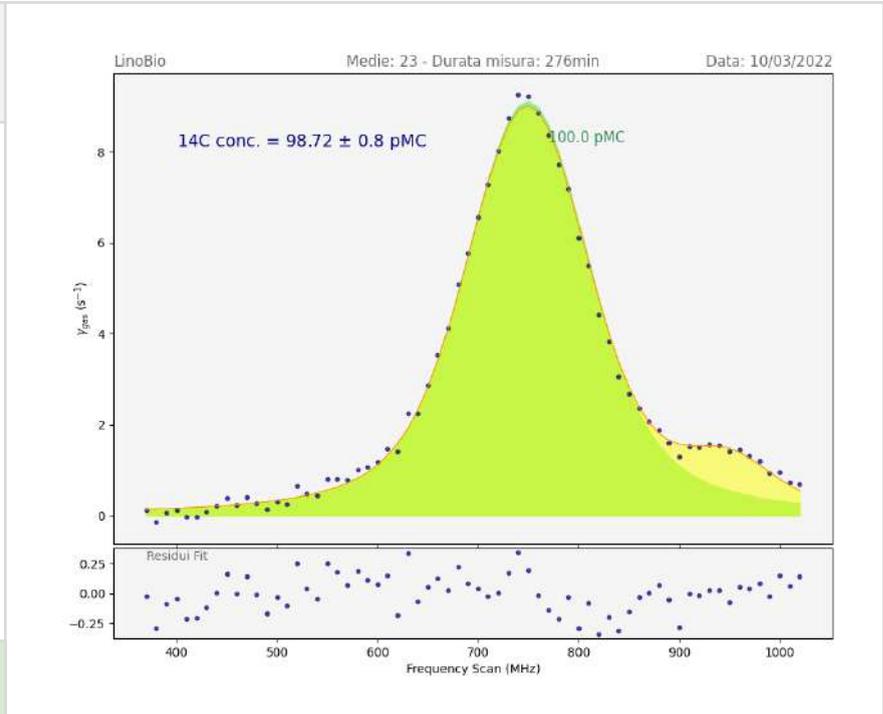
Chemical products

Product for leather tanning
courtesy of ArsTinctoria

Result: 85% bio

0113 Medie: 10 - Durata misura: 60min Data: 21/01/2022

14C conc. = 85.08 ± 0.9 pMC 100.0 pMC

Residui Fit

Leather and synthetic leather

"Bio" leather
courtesy of ArsTinctoria

Campione: AN04116-21_1   Medie: 14 - Durata misura: 90min   Data: 21/07/2021

14C conc. = 45.07 ± 0.90 pMC   100% BIO

Result: 45% bio

True leather
courtesy of ArsTinctoria

0922_2   Medie: 10 - Durata misura: 60min   Data: 23/02/2022

14C conc. = 99.43 ± 1.1 pMC   100.0 pMC

Result: 99% bio

Footwear materials

Shoe upper
courtesy of ArsTinctoria

7017-21
Tomaio Beige

Result: 33% bio

7017TomBei   Medie: 10 - Durata misura: 60min   Data: 27/01/2022
100.0 pMC
14C conc. = 33.46 ± 1.3 pMC
V_{gas} (s⁻¹)
Residui Fit
Frequency Scan (MHz)
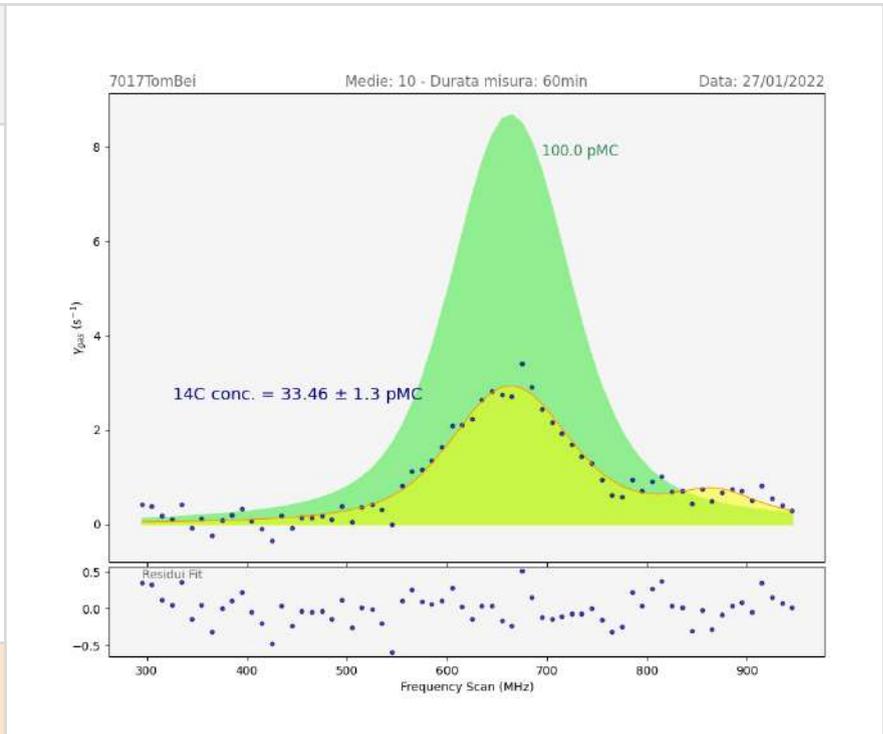
Shoe sole
courtesy of ArsTinctoria

7017-21
Suole.

Result: 1.5% bio

7018Suo   Medie: 10 - Durata misura: 60min   Data: 28/01/2022
100.0 pMC
14C conc. = 1.50 ± 1.4 pMC
V_{gas} (s⁻¹)
Residui Fit
Frequency Scan (MHz)

Nuclear waste material

Graphite from nuclear power plant
courtesy of JRC of Karlsruhe (DE)

Result: 31 x modern

14C conc. = 3127.06 ± 5.1 pMC

100.0 pMC
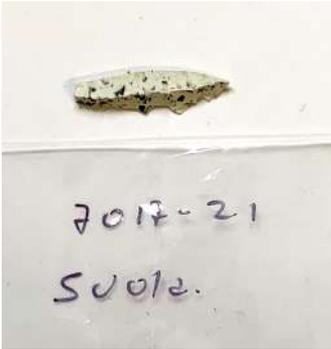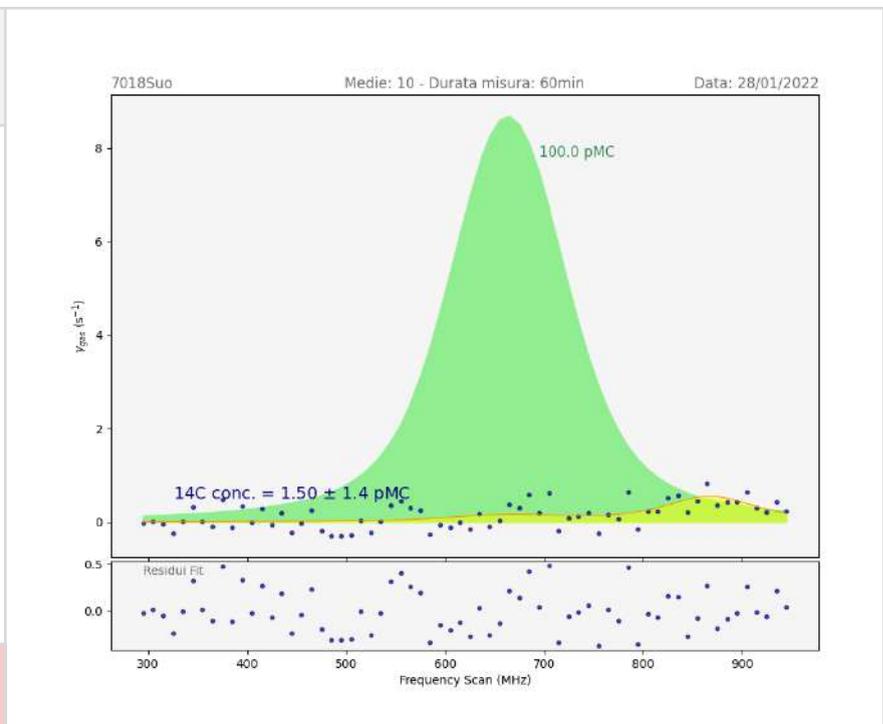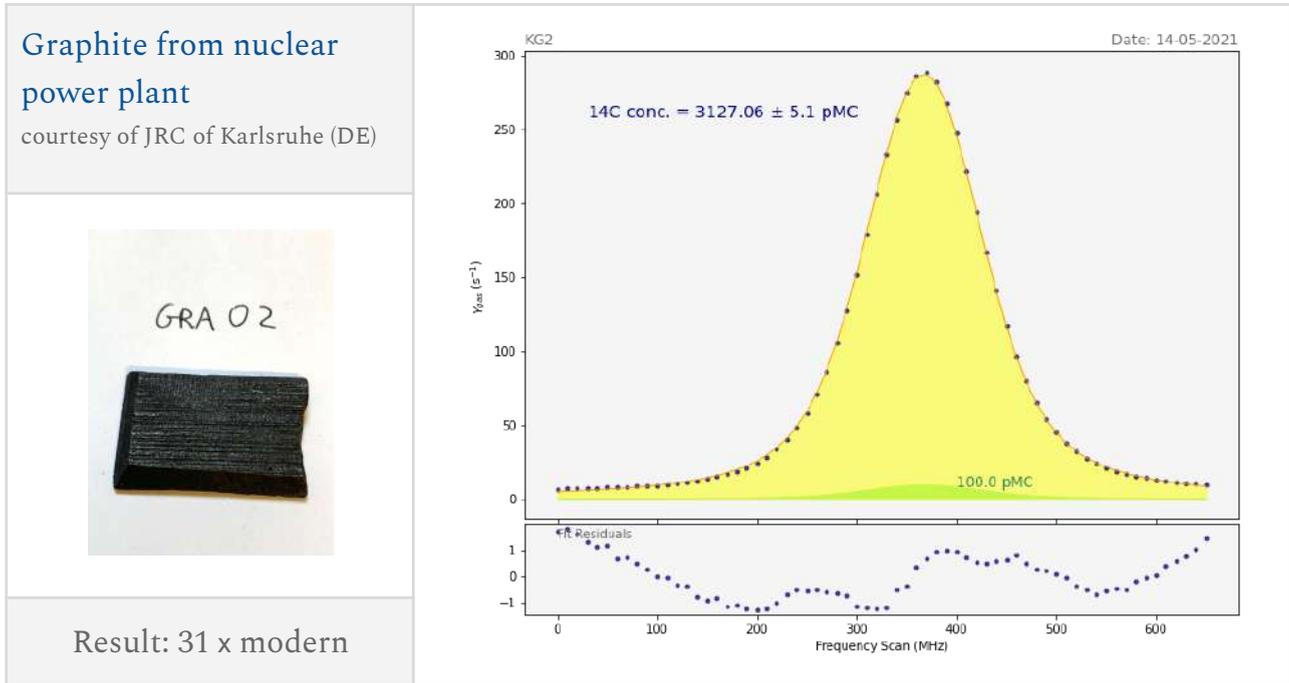
Biological material for new drug development

^{14}C-enriched urine
courtesy of Sivvon Science (Korea)

Result: 1031 x modern

14C conc. = 103109.89 ± 80.0 pMC

100.0 pMC
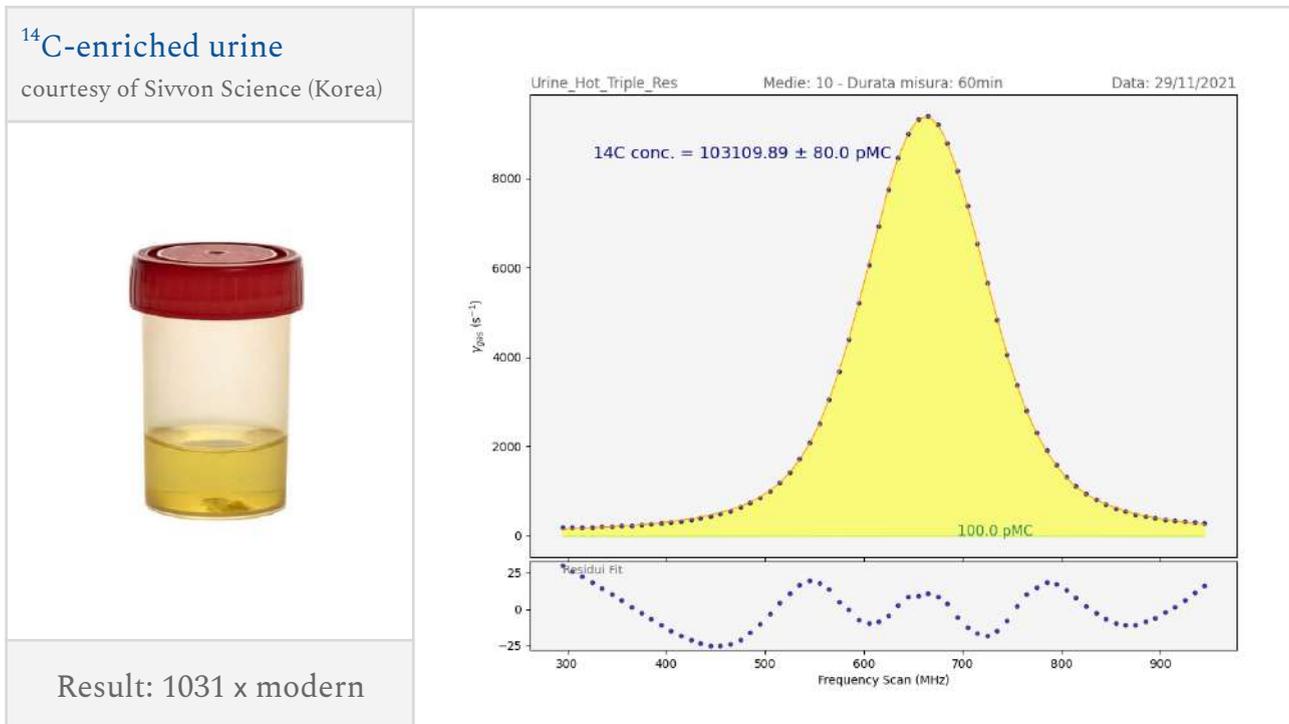
Performances of the instrument

Repeatability and ultimate sensitivity

Long-averaging measurements are useful not only to improve the precision, but also to study the repeatability of the technique.

In the following, results obtained by our **prototype instrument** are presented. A very long series of acquisitions taken over several days during 2 weeks on a standard sample of Oxalic Acid and with the same instrument is presented and analyzed. The ^{14}C concentration in the Oxalic Acid standard is **134.07 pMC**. The total number of 6min-long measurements is 401, corresponding to a total measurement time of about 40 hours.
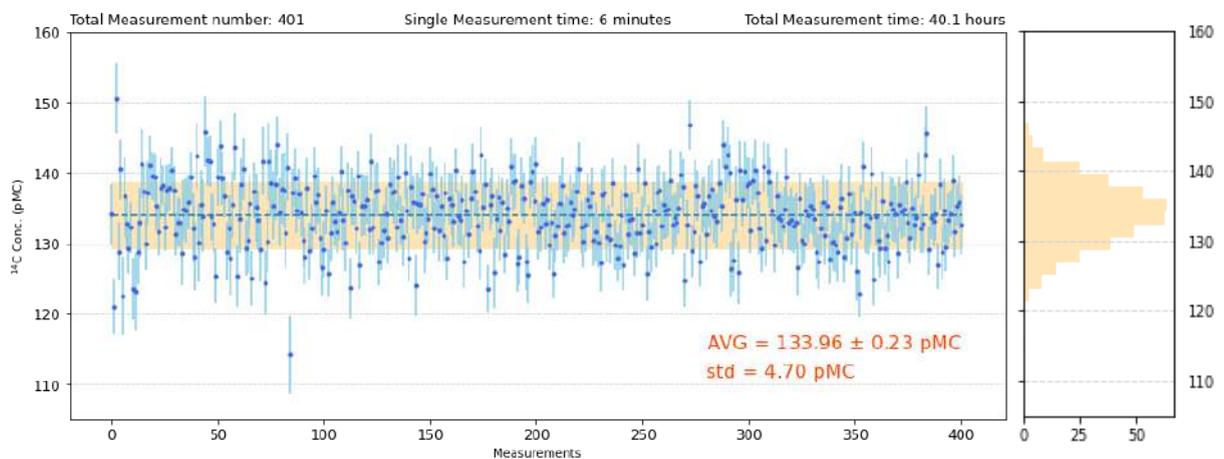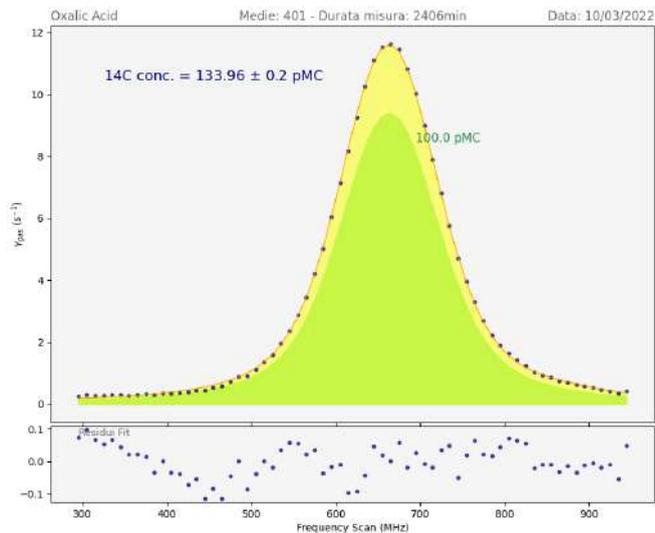
The above analysis gives several informations about the repeatability of the measurement. First of all it shows how measurements taken on the same sample and on the same instrument are replicable over a quite long period of time (2 weeks in this case).

Secondly, the standard deviation (σ) of the measurements gives the repeatability error of the 6min-long acquisition. In the same way, by grouping the acquisition by 2, 3 etc., the repeatability of longer averaging measurements can be retrieved. These results are shown in the table below:

Repeatability Error	
Averaging Time	σ (pMC)
6 min	4.7
12 min	3.3
18 min	2.6
24 min	2.3
30 min	2.0
1 h	1.4
2 h	1.2
4 h	0.9
8 h	0.8
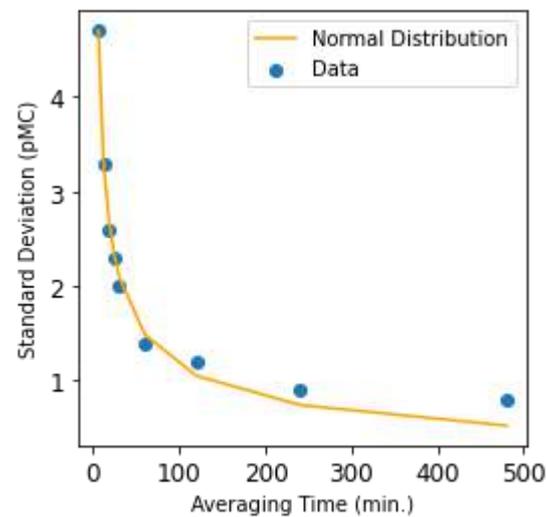
Moreover, the values are normally distributed, as shown by the histogram and by the dependence of σ on the averaging time. Only for averaging times > 2hours there is a significant discrepancy between the data and the expected behavior, suggesting that some other non-statistical noise source becomes important below the 1pMC error threshold.

Nevertheless, a full average over the whole data set leads to an ultimate standard error of the mean of about 0.2 pMC, that is comparable with the best results ever obtained by the AMS competitor technology.

Constant improvement of performances

The performances of C14-SCAR are improving together with the development of the instrument. The technological efforts in standardizing the production and re-engineering all the parts of the machine are bringing evident improvements both on precision and repeatability.
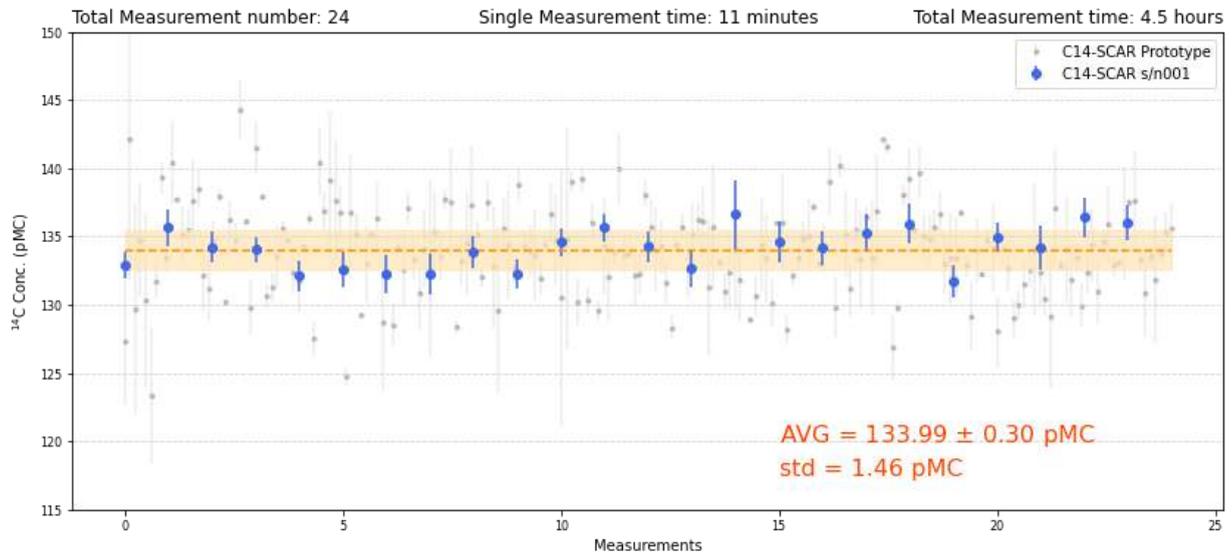
The graph above shows a comparison between the measurement series presented in the previous section (taken with the prototype instrument) and a series of 24 measurements taken with the first commercialized instrument at the customer site.

The improvements achieved by the s/n001 are resumed in the table below, in terms of achieved precision.
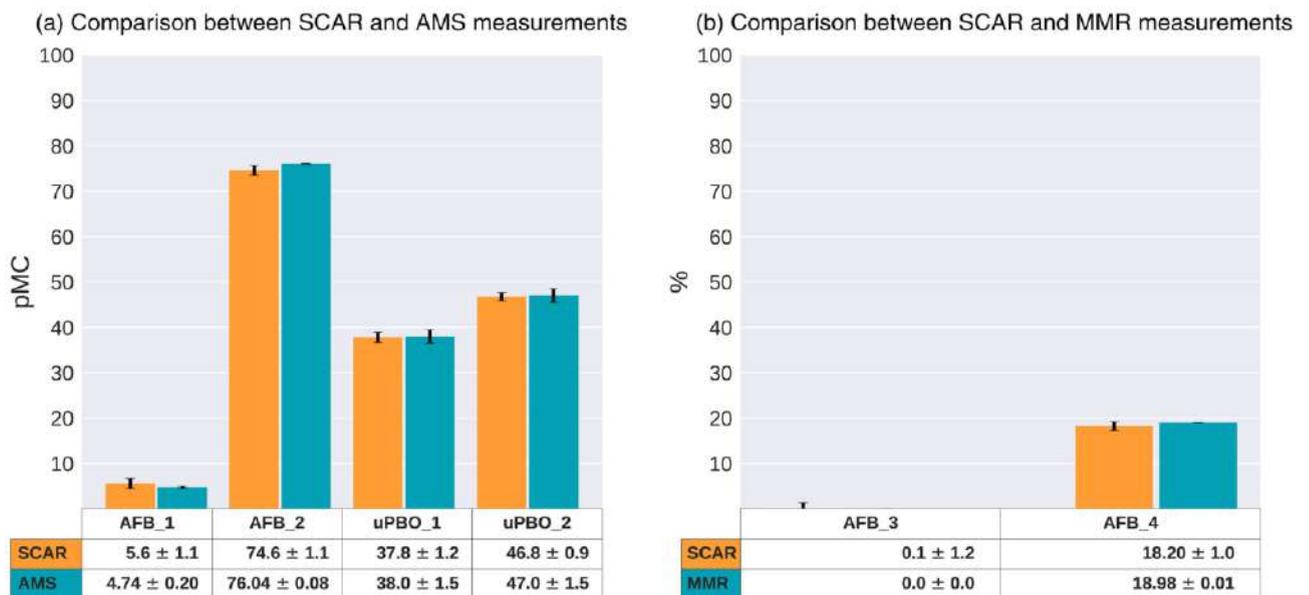
Averaging time (min)	Achieved Precision (pMC)	
	Prototype	s/n001
12	3.3	1.5
24	2.3	1.1
60	1.4	0.8
240	0.9	0.3

Comparison with existing methods: AMS

The use of ^{14}C as a biogenic marker has proven to be effective and reliable for the high analytical selectivity and because no a priori information on the sample is required. Nowadays, only two well-established techniques, accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC), can also rely on the direct assessment of the ^{14}C content to measure the biogenic fraction in any kind of fuel. In particular, AMS can achieve uncertainty values in measuring the biogenic content of different fuel blends ranging between 0.3% and 1% for liquids, and 0.7–4.5% for gasses. LSC can achieve uncertainty values of 0.2–4% in measuring the biogenic content of liquid fuels and cannot be used for gas phase samples.

Comparison on fuel samples

(a) Comparison between SCAR and AMS measurements				(b) Comparison between SCAR and MMR measurements		
	AFB_1	AFB_2	uPBO_1	uPBO_2	AFB_3	AFB_4
SCAR	5.6 ± 1.1	74.6 ± 1.1	37.8 ± 1.2	46.8 ± 0.9	0.1 ± 1.2	18.20 ± 1.0
AMS	4.74 ± 0.20	76.04 ± 0.08	38.0 ± 1.5	47.0 ± 1.5		
MMR					0.0 ± 0.0	18.98 ± 0.01

We show above the results of the analysis of six samples, namely, blends of HEFA aviation fuel with Jet A-1 fossil fuel and bio-oil derived from pyrolyzed biomass, to demonstrate the accuracy achieved by the SCAR technique in the determination of the biogenic fraction in fuel blends. This accuracy evaluation was performed by using both AMS, as primary verification method, and direct mass mixing ratio (MMR), as independent cross-check. Indeed, the measured ^{14}C contents of avionic fuel blends AFB_1, AFB_2 (provided by Neste Corporation) and upgraded pyrolysis bio-oil uPBO_1, uPBO_2 (provided by RISE: Research Institute of Sweden) were compared to the AMS results, with the aim of proving the accuracy of the SCAR technology. Afterward, avionic fuel blends AFB_3 and AFB_4 (provided by CSV-AM: Centro Sperimentale di Volo, Aeronautica

Militare), prepared with fixed biogenic/fossil composition by mixing precisely measured mass ratios, were analyzed using the SCAR technique.

To obtain an estimate of the ^{14}C content in each sample, a relative measurement must be performed by comparing it with a standard reference material. Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$) provided by National Institute of Standards and Technology (SRM 4990C), with a carbon mass content of 19% and a ^{14}C content of 134.07 pMC, was chosen as a reference for samples AFB_1, AFB_2, uPBO_1, and uPBO_2, in accordance with the well-established protocol used for AMS measurements.

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